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Synergistically active herbicidal mixtures

The present invention relates to a synergistically active herbicidal mixture composed of a sulfonylurea derivative (a) of the formula I and one or more herbicidal compounds b1 to b41.

Herbicidally active sulfonylureas of the formula I have been disclosed in the prior art, for example in EP-388 873, EP-559 814, EP-291 851 and DE-40 07 683 and the Conference Proceedings "Fluorine in Agriculture", January 9-11 1995, Manchester, chapter "New Fluoro Intermediates for Herbicidal Sulfonylureas".

Herbicidal compounds b1 to b41 are described, for example, in

15 "Herbizide", Hock, Fedtke, Schmidt, 1st Edition, Thieme 1995 (see "quinclorac" p. 238, "molinate" p. 32, "butachlor" p. 32, "pretilachlor" p. 32, "dithiopyr" p. 32, "mefenacet" p. 32, "fenoxapropethyl" p. 216, "dimepiperate" p. 32, "pyrazolate" p. 146, "pyrazoxyfen" p. 146, "bensulfuron-methyl" p. 31,

20 "pyrazosulfuron-ethyl" p. 31, "cinosulfuron" p. 31, "benfuresate" p. 233, "bromobutide" p. 243, "dymrone" p. 243, "dimethyametryn" p. 118, "esprocarb" p. 229, "pyributicarb" p. 32, "cinemthylin" p. 32, "propanil" p. 32, "2,4-D" p. 30, "bentazone" p. 30, "DPX-A-8947" p. 175, "mecoprop-P" p. 237, "chlorpropham" p. 205,

25 "thiocarbazil" p. 229, "ethoxyfen" p. 30, "haloxyfop-P-methyl" p. 38, "haloxyfop-ethoxyethyl" p. 38, "flumiclorac-pentyl" p. 35, "flupropacil" p. 143, "nipyraclufen" p. 145, "metosulam" p. 33, "ethametsulfuron-methyl" p. 36, "thifensulfuron-methyl" p. 35 or in

30 "Agricultural Chemicals", Book II Herbicides, 1993 see "thiobencarb" p. 85, "benzofenap" p. 221, "napropanilid" p. 49, "piperophos" p. 102, "anilofos" p. 241, "TH-913" p. 150, "HW-52" p. 54, "ICIA-0051" p. 268, "poast" p. 253, "focus" p. 222, "dimethenamid" p. 48, "sulfosate" p. 236, "2,4-DB" p. 10,

35 "dichlorprop-P" p. 6, "flupoxam" p. 44, "prosulfocarb" p. 84, "quinmerac" p. 233, "metazachlor" p. 64, "flurtamone" p. 265, "bromofenoxim" p. 228, "fomesafen" p. 248, "imazethabenz-methyl" p. 153, "clodinafop" p. 214, "fenoxaprop-P-ethyl" p. 208, "fluazifop-P-butyl" p. 207, "quizalofop-P-ethyl" p. 210,

40 "quizalofop-terfuryl" p. 211, "flumioxazin" p. 43, "flumipropyn" p. 267, "sulfentrazone" p. 261, "thiazopyr" p. 226, "pyrithiobac-sodium" p. 266, "flumetsulam" p. 227, "amidosulfuron" p. 151, "halosulfuron-methyl" p. 148, "rimsulfuron" p. 138, "tribenuron-methyl" p. 139,

45 "triflusaluron-methyl" p. 137, "primisulfuron" p. 147 or in

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- "Short Review of Herbicides & PGRs 1991, Hodogaya Chemicals see
 "furyloxyfen" p. 142, "triazofenamid" p. 268, "KH-218" p. 52,
 "NSK-850" p. 52, "JC-940" p.90, "AC-92553" p. 58, "buthidazole"
 p. 88, "cyprazole" p.38, "allidochlor" p. 48, "benzoylprop-ethyl"
 5 p. 38, "chlorthiamid" p. 150, "diphenamid" p. 34,
 "flamprop-methyl" p. 40, "fosamin" p. 232, "isoxaben" p. 42,
 "monalide" p. 32, "naptalam" p. 36, "pronamid" p. 34, "bialaphos"
 p. 234, "glufosinate-ammonium" p. 234, "glyphosate" p. 232,
 "amitrol" p. 254, "clomeprop" p. 20, "dichlorprop" p. 6,
 10 "fenoprop" p. 8, "fluroxypyr" p. 156, "MCPA" p. 4, "MCPB" p. 8,
 "mecoprop" p. 6, "napropamide" p. 16, "triclopyr" p. 154,
 "chloramben" p. 28, "dicamba" p. 26, "clomazone" p. 268,
 "diflufenican" p. 42, "fluorochloridone" p. 266, "fluridone" p.
 156, "asulam" p. 112, "barban" p. 100, "butylate" p. 106,
 15 "carbetamide" p. 36, "chlorobufam" p. 100, "cycloate" p. 108,
 "desmedipham" p. 104, "di-allate" p. 106, "EPTC" p. 108,
 "orbencarb" p. 112, "pebulate" p. 106, "phenisopham" p. 118,
 "pendimedipham" p. 104, "propham" p. 100, "sulf-allate" p. 110,
 "terbucarb" p. 102, "tri-allate" p. 108, "vernolate" p. 108,
 20 "acetochlor" p. 48, "alachlor" p. 46, "diethathyl-ethyl" p. 48,
 "dimethachlor" p. 50, "metolachlor" p. 46, "propachlor" p. 44,
 "pyrnachlor" p. 44, "terbuchlor" p. 48, "xylachlor" p. 52,
 "alloxydim" p. 260, "clethodim" p. 270, "cloproxydim" p. 268,
 "tralkoxydim" p. 270, "dalapon" p. 212, "ethofumesate" p. 124,
 25 "benefin" p. 54, "butralin" p. 58, "dinitramin" p. 56,
 "ethalfluralin" p. 60, "fluchloralin" p. 54, "isopropalin" p. 58,
 "nitralin" p. 58, "oryzalin" p. 60, "prodiamine" p. 62,
 "profluralin" p. 54, "trifluralin" p. 54, "dinoseb" p. 128,
 "dinoseb-acetate" p. 128, "dinoterb" p. 128, "DNOC" p. 126,
 30 "acilfluorfen-sodium" p. 142, "aclonifen" p. 146, "bifenox" p.
 140, "chlornitrofen" p. 138, "difenoxuron" p. 76, "fluorodifen"
 p. 138, "fluoroglycofen-ethyl" p. 146, "lactofen" p. 144,
 "nitrofen" p. 136, "nitrofluorfen" p. 140, "oxyfluorfen" p. 140,
 "cyperquat" p. 158, "difenzoquat" p. 160, "diquat" p. 158,
 35 "paraquat" p. 158, "benzthiazuron" p. 82, "buturon" p. 66,
 "chlorbromuron" p. 72, "chloroxuron" p. 76, "chlortoluron" p. 74,
 "cycluron" p. 84, "dimeturon" p. 88, "diuron" p. 70,
 "ethidimuron" p. 86, "fenuron" p. 64, "fluometuron" p. 68,
 "isoproturon" p. 80, "isouron" p. 88, "karbutilate" p. 76,
 40 "linuron" p. 72, "methabenzthiazuron" p. 82, "metoxuron" p. 72,
 "monolinuron" p. 66, "monuron" p. 64, "neburon" p. 72, "siduron"
 p. 68, "tebuthiuron" p. 86, "trimeturon" p. 64, "isocarbamid" p.
 168, "imazamethapyr" p. 172, "imazapyr" p. 170, "imazaquin" p.
 170, "imazethapyr" p. 172, "methazole" p. 162, "oxadiazon" p.
 45 162, "tridiphane" p. 266, "bromoxynil" p. 148, "ioxynil" p. 148,
 "diclofop-methyl" p. 16, "fenthiaprop-ethyl" p. 20,
 "fluazifop-butyl" p. 18, "haloxyfop-methyl" p. 18, "isoxapyrifop"

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- p. 22, "propaquizafop" p. 24, "quizalofop-ethyl" p. 20,
 "chlorfenac" p. 258, "chlorophenprop-methyl" p. 258,
 "chloridazon" p. 174, "maleic hydrazide" p. 162, "norflurazon" p.
 174, "pyridate" p. 176, "clopyralid" p. 154, "picloram" p. 154,
 5 "chlorimuron-ethyl" p. 92, "chlorsulfuron" p. 92, "flazasulfuron"
 p. 96, "metsulfuron-methyl" p.92, "nicosulfuron" p. 96,
 "sulfometuron-methyl" p. 92, "triasulfuron" p. 94, "ametryn" p.
 198, "atrazine" p. 188, "aziprotryne" p. 206, "cyanazine" p. 192,
 "cyprazine" p. 192, "desmetryne" p. 200, "dipropetryn" p. 202,
 10 "eglinazine-ethyl" p. 208, "hexazinon" p. 208, procyazine" p.
 192, "prometone" p. 196, "prometryn" p. 196, "propazine" p. 188,
 "secbumeton" p. 196, "simazine" p. 188, "simetryn" p. 196,
 "terbumeton" p. 204, "terbutryn" p. 198, "terbuthylazine" p. 190,
 "trietazine" p. 188, "ethiozin" p. 210, "metamitron" p. 206,
 15 "metribuzin" p. 202, "bromacil" p. 180, "lenacil" p. 180,
 "terbacil" p. 180, "benazolin" p. 262, "bensulide" p. 228,
 "benzofluor" p. 266, "butamifos" p. 228, "DCPA" p. 28,
 "dichlobenil" p. 148, "endothal" p. 264, "mefluidide" p. 306,
 "perfluidone" p. 260, "terbuchlor" p. 48 or in
 20 "Global Herbicide Directory" First Edition, 1994 see "oxadiargyl"
 p. 96, or in "European Directory of Agrochemical Products Volume
 2 - Herbicides" Fourth Edition, see "buminafos" p. 255. The
 compound "DEH-112" is disclosed in European Patent Application
 EP 0 302 203. The compound "caloxydim" is described in
 25 DE 3 336 140, the compound "cinidon-ethyl" in DE 3 603 789 and
 the compound "fluorbentranyl" in EP 84 893. Other compounds are
 known from "Brighton Crop Protection Conference - Weeds - 1993
 (see "thidiazimin" p. 29, "AC-322140" p. 41, "KIH-6127" p. 47,
 "prosulfuron" p. 53, "KIH-2023" p. 61, "metobenzuron" p. 67). The
 30 compound "CH-900" is described in EP 0 332 133.

In principle, it is desirable in crop protection products to
 increase the specific activity of an active ingredient and the
 reliability of its action. It was therefore the object of the
 35 present invention to increase the activity of known, herbicidally
 active sulfonylureas of the formula I.

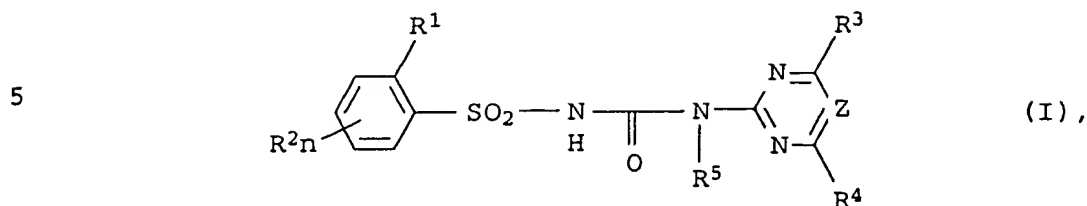
We have found that this object is achieved by a herbicidal mix-
 ture which comprises

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a) at least one derivative of the sulfonylurea of the formula I



10 where the substituents have the following meanings:

R¹ is C₁-C₆-alkyl which has attached to it one to five of the following groups: methoxy, ethoxy, SO₂CH₃, cyano, chlorine, fluorine, SCH₃, S(O)CH₃;

15

halogen;

a group ER⁶ where E is O, S or NR⁷;

20

COOR⁸;

NO₂;

S(O)₂R⁹, SO₂NR¹⁰R¹¹, CONR¹⁰R¹¹;

25

R² is hydrogen, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, halogen, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy; C₁-C₄-haloalkyl, a C₁-C₂-alkylsulfonyl group, nitro, cyano or C₁-C₄-alkylthio;

30

R³ is F, CF₃, CF₂Cl, CF₂H, OCF₃, OCF₂Cl, or, if R¹ is CO₂CH₃ and R² is simultaneously fluorine, R³ is Cl, or, if R¹ is CH₂CF₃ or CF₂CF₃, R³ is methyl, or, if R⁴ is OCF₃ or OCF₂Cl, R³ is OCF₂H or OCF₂Br;

35

R⁴ is C₁-C₂-alkoxy, C₁-C₂-alkyl, C₁-C₂-alkylthio, C₁-C₂-alkylamino, di-C₁-C₂-alkylamino, halogen, C₁-C₂-haloalkyl, C₁-C₂-haloalkoxy,

40

R⁵ is hydrogen, C₁-C₂-alkoxy, C₁-C₄-alkyl;

R⁶ is C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl or C₃-C₆-cycloalkyl, all of which can have attached to them 1 to 5 halogen atoms, with the exception of allyl, difluoromethoxy, chlorodifluoromethoxy and 2-chloroethoxy, if E is O or S. In the event that E is O or NR⁷, R⁶ is furthermore also methylsulfonyl,

45

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ethylsulfonyl, trifluoromethylsulfonyl, allylsulfonyl, propargylsulfonyl or dimethylsulfamoyl;

R⁷ is hydrogen, methyl or ethyl

5

R⁸ is a C₁-C₆-alkyl group which can have attached to it up to three of the following radicals: halogen, C₁-C₄-alkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₂-alkoxy, C₃-C₇-cycloalkyl and/or phenyl; a C₅-C₇-cycloalkyl group which can have attached to it up to three C₁-C₄-alkyl groups; C₃-C₆-alkenyl or C₃-C₆-alkynyl;

10

R⁹ is a C₁-C₆-alkyl group which can have attached to it one to three of the following radicals: halogen, C₁-C₄-alkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₂-alkoxy, C₃-C₇-cycloalkyl and/or phenyl; a C₅-C₇-cycloalkyl group which can have attached to it one to three C₁-C₄-alkyl groups; a C₃-C₆-alkenyl group or a C₃-C₆-alkynyl group;

15

20

R¹⁰ is hydrogen, a C₁-C₂-alkoxy group, a C₁-C₆-alkyl group, or together with R¹¹ is a C₄-C₆-alkylene chain in which one methylene group can be replaced by an oxygen atom or a C₁-C₄-alkylimino group;

25

R¹¹ is a C₁-C₄-alkyl group which can have attached to it one to four halogen or C₁-C₄-alkoxy radicals; C₃-C₆-cycloalkyl

30

n is 0 - 3

o is 1 - 2

Z N or CH,

35

and

b) a synergistically active amount of at least one herbicidal compound selected from the groups b1 to b41

40

b1 1,3,4-thiadiazoles:
buthidazole, cyprazole

b2 amides:

45

allidochlor (CDAA), benzoylprop-ethyl, bromobutide, chlorthiamid, dimepiperate, dimethenamid, diphenamid, etobenzanid (benzchlomet), flamprop-methyl, fosamin,

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isoxaben, monalide, naptalame, pronamid (propyzamid),
propanil

- 5 b3 aminophosphoric acids:
 bilanafos, (bialaphos), buminafos, glufosinate-ammonium,
 glyphosate, sulfosate
- 10 b4 aminotriazoles:
 amitrol
- b5 anilides:
 anilofos, mefenacet
- 15 b6 aryloxyalkanoic acids:
 2,4-D, 2,4-DB, clomeprop, dichlorprop, dichlorprop-P,
 dichlorprop-P (2,4-DP-P), fenoprop (2,4,5-TP), fluoroxy-
 pyr, MCPA, MCPB, mecoprop, mecoprop-P, napropamide,
 napropanilide, triclopyr
- 20 b7 benzoic acids:
 chloramben, dicamba
- b8 benzothiadiazinones:
 bentazone
- 25 b9 bleaches:
 clomazone (dimethazone), diflufenican, fluorochloridone,
 flupoxam, fluridone, pyrazolate, sulcotrione (chlormesu-
 lone)
- 30 b10 carbamates:
 asulam, barban, butylate, carbetamid, chlorbufam, chlor-
 propham, cycloate, desmedipham, di-allate, EPTC, espro-
 carb, molinate, orbencarb, pebulate, phenisopham, phenme-
35 dipham, propham, prosulfocarb, pyributicarb, sulf-allate
 (CDEC), terbucarb, thiobencarb (benthicarb), tiocarba-
 zil, tri-allate, vernolate
- 40 b11 quinolinecarboxylic acids:
 quinclorac, quinmerac
- 45 b12 chloracetanilides:
 acetochlor,alachlor, butachlor, butenachlor, diethatyl-
 ethyl, dimethachlor, metazachlor, metolachlor, pretilach-
 lor, propachlor, prynachlor, terbuchlor, thenylchlor,
 xylachlor

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- b13 cyclohexenones:
alloxydim, caloxydim, clethodim, cloproxydim, cycloxydim,
sethoxydim, tralkoxydim, 2-{1-[2-(4-
chlorophenoxy)propyloxyimino]butyl}-3-hydroxy-5-(2H-
5 tetrahydrothiopyran-3-yl)-2-cyclohexen-1-one
- b14 dichloropropionic acids:
dalapon
- 10 b15 dihydrobenzofurans:
ethofumesate
- b16 dihydrofuran-3-ones:
flurtamone
- 15 b17 dinitroanilines:
benefin, butralin, dinitramin, ethalfluralin, fluchlora-
lin, isopropalin, nitratin, oryzalin, pendimethalin, pro-
diamine, profluralin, trifluralin
- 20 b18 dinitrophenols:
bromofenoxim, dinoseb, dinoseb-acetate, dinoterb, DNOC
- b19 diphenyl ethers:
25 acifluorfen-sodium, aclonifen, bifenox, chlornitrofen
(CNP), difenoxuron, ethoxyfen, fluorodifen, fluoroglyc-
ofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen,
nitrofluorfen, oxyfluorfen
- 30 b20 dipyridylenes:
cyperquat, difenzoquat methylsulfate, diquat, paraquat
dichloride
- b21 ureas:
35 benzthiazuron, buturon, chlorbromuron, chloroxuron,
chlortoluron, cumyluron, dibenzyluron, cycluron, dimefu-
ron, diuron, dymrone, ethidimuron, fenuron, fluometuron,
isoproturon, isouron, karbutilate, linuron, methabenz-
thiazuron, metobenzuron, metoxuron, monolinuron, monuron,
40 neburon, siduron, tebuthiuron, trimeturon
- b22 imidazoles:
isocarbamid

- b23 imidazolinones:
imazamethapyr, imazapyr, imazaquin, imazethabenz-methyl
(imazame), imazethapyr
- 5 b24 oxadiazoles:
methazole, oxadiargyl, oxadiazon
- b25 oxiranes:
tridiphane
- 10 b26 phenols:
bromoxynil, ioxynil
- 15 b27 phenoxyphenoxypropionic esters:
clodinafop, cyhalofop-butyl, diclofop-methyl, fenoxaprop-
ethyl, fenoxaprop-P-ethyl, fenthiapropethyl, fluazifop-
butyl, fluazifop-P-butyl, haloxyfop-ethoxyethyl, haloxy-
fop-methyl, haloxyfop-P-methyl, isoxapyrifop, propaquiza-
fop, quizalofop-ethyl, quizalofop-P-ethyl, quizalofop-
20 tefuryl
- b28 phenylacetic acids:
chlorfenac (fenac)
- 25 b29 phenylpropionic acid:
chlorophenprop-methyl
- b30 protoporphyrinogen IX oxydase inhibitors:
benzofenap, cinidon-ethyl, flumiclorac-pentyl, flumioxa-
zin, flumipropyn, flupropacil, fluthiacet-methyl, pyrazo-
xyfen, sulfentrazone, thidiazimin
- 30 b31 pyrazoles:
nipyraclufen
- 35 b32 pyridazines:
chloridazon, maleic hydrazide, norflurazon, pyridate
- b33 pyridinecarboxylic acids:
40 clopyralid, dithiopyr, picloram, thiazopyr
- b34 pyrimidyl ethers:
pyrithiobac acid, pyrithiobac sodium, KIH-2023, KIH-6127
- 45 b35 sulfonamides:
flumetsulam, metosulam

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- 5 b36 sulfonylureas:
 amidosulfuron, azimsulfuron, bensulfuron-methyl, chlori-
 muron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamu-
 ron, ethametsulfuron-methyl, ethoxysulfuron, flazasulfu-
 ron, halosulfuron-methyl, imazosulfuron, metsulfuron-
 methyl, nicosulfuron, primisulfuron, prosulfuron, pyrazo-
 sulfuron-ethyl, rimsulfuron, sulfometuron-methyl, thifen-
 sulfuron-methyl, triasulfuron, tribenuron-methyl, triflu-
 sulfuron-methyl
- 10 b37 triazines:
 ametryn, atrazine, aziprotryn, cyanazine, cyprazine, des-
 metryn, dimethamethryn, dipropetryn, eglinazine-
 ethyl, hexazinon, procyazine, prometon, prometryn,
 15 propazine, secbumeton, simazine, simetryn, terbumeton,
 terbutryn, terbuthylazine, trietazine
- b38 triazinones:
 ethiozin, metamitron, metribuzin
- 20 b39 triazolecarboxamides:
 triazofenamid
- b40 uracils:
 25 bromacil, lenacil, terbacil
- b41 others:
 benazolin, benfuresate, bensulide, benzofluor, butamifos,
 cafenstrole, chlorthal-dimethyl (DCPA), cinmethylin,
 30 dichlobenil, endothall, fluorbentrail, mefluidide, per-
 fluidone, piperophos

or their environmentally compatible salts.

- 35 The herbicidal mixture according to the invention has superaddi-
 tive synergistic action and is selective for those crop plants
 which also tolerate the individual compounds themselves.

Especially preferred sulfonylureas of the formula I with a view
 40 to their synergistic herbicidal action are those where

R^1 is CO_2CH_3 , $CO_2C_2H_5$, $CO_2iC_3H_7$, CF_3 , CF_2H ; OSO_2CH_3 , $OSO_2N(CH_3)_2$,
 Cl , NO_2 , $SO_2N(CH_3)_2$, SO_2CH_3 and $N(CH_3)SO_2CH_3$

- 45 R^2 is hydrogen, Cl , F or C_1 - C_2 -alkyl

R^3 is CF_2H , OCF_3 , OCF_2Cl , CF_2Cl , CF_3 or F

R^4 is OCH_3 , OC_2H_5 , OCF_3 , OCF_2Cl ; CF_3 , Cl , F , $NH(CH_3)$, $N(CH_3)_2$ or C_1 - C_2 -alkyl

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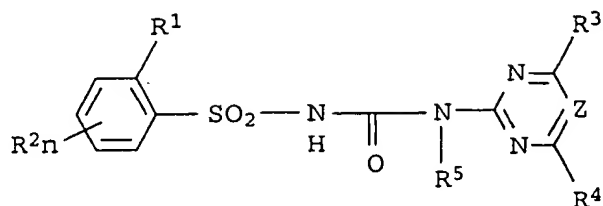
R^5 is hydrogen,

Z N or CH and

10 n 0 or 1.

Preferred compounds of the formula I are compiled in the table which follows.

15 Table



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40

45

No.	R^1	R^2	R^5	R^3	R^4	Z
1	CO_2CH_3	H	H	OCF_2Cl	OCH_3	CH
2	$CO_2C_2H_5$	H	H	OCF_2Cl	OCH_3	CH
3	$CO_2iC_3H_7$	H	H	OCF_2Cl	OCH_3	CH
4	NO_2	H	H	OCF_2Cl	OCH_3	CH
5	SO_2CH_3	H	H	OCF_2Cl	OCH_3	CH
6	$SO_2N(CH_3)_2$	H	H	OCF_2Cl	OCH_3	CH
7	Cl	H	H	OCF_2Cl	OCH_3	CH
8	$N(CH_3)SO_2CH_3$	H	H	OCF_2Cl	OCH_3	CH
9	OSO_2CH_3	H	H	OCF_2Cl	OCH_3	CH
10	$OSO_2N(CH_3)_2$	H	H	OCF_2Cl	OCH_3	CH
11	CF_3	H	H	OCF_2Cl	OCH_3	CH
12	CF_2H	H	H	OCF_2Cl	OCH_3	CH
13	CO_2CH_3	H	H	OCF_3	OCH_3	CH
14	$CO_2C_2H_5$	H	H	OCF_3	OCH_3	CH
15	$CO_2iC_3H_7$	H	H	OCF_3	OCH_3	CH
16	NO_2	H	H	OCF_3	OCH_3	CH

No.	R ¹	R ²	R ⁵	R ³	R ⁴	Z
17	SO ₂ CH ₃	H	H	OCF ₃	OCH ₃	CH
18	SO ₂ N(CH ₃) ₂	H	H	OCF ₃	OCH ₃	CH
19	Cl	H	H	OCF ₃	OCH ₃	CH
20	N(CH ₃) SO ₂ CH ₃	H	H	OCF ₃	OCH ₃	CH
21	OSO ₂ CH ₃	H	H	OCF ₃	OCH ₃	CH
22	OSO ₂ N(CH ₃) ₂	H	H	OCF ₃	OCH ₃	CH
23	CF ₃	H	H	OCF ₃	OCH ₃	CH
24	CF ₂ H	H	H	OCF ₃	OCH ₃	CH
25	CO ₂ CH ₃	H	H	F	OCH ₃	CH
26	CO ₂ C ₂ H ₅	H	H	F	OCH ₃	CH
27	CO ₂ iC ₃ H ₇	H	H	F	OCH ₃	CH
28	NO ₂	H	H	F	OCH ₃	CH
29	SO ₂ CH ₃	H	H	F	OCH ₃	CH
30	SO ₂ N(CH ₃) ₂	H	H	F	OCH ₃	CH
31	Cl	H	H	F	OCH ₃	CH
32	N(CH ₃) SO ₂ CH ₃	H	H	F	OCH ₃	CH
33	OSO ₂ CH ₃	H	H	F	OCH ₃	CH
34	OSO ₂ N(CH ₃) ₂	H	H	F	OCH ₃	CH
35	CF ₃	H	H	F	OCH ₃	CH
36	CF ₂ H	H	H	F	OCH ₃	CH
37	CO ₂ CH ₃	H	H	CF ₃	OCH ₃	N
38	CO ₂ C ₂ H ₅	H	H	CF ₃	OCH ₃	N
39	CO ₂ iC ₃ H ₇	H	H	CF ₃	OCH ₃	N
40	NO ₂	H	H	CF ₃	OCH ₃	N
41	SO ₂ CH ₃	H	H	CF ₃	OCH ₃	N
42	SO ₂ N(CH ₃) ₂	H	H	CF ₃	OCH ₃	N
43	Cl	H	H	CF ₃	OCH ₃	N
44	N(CH ₃) SO ₂ CH ₃	H	H	CF ₃	OCH ₃	N
45	OSO ₂ CH ₃	H	H	CF ₃	OCH ₃	N
46	OSO ₂ N(CH ₃) ₂	H	H	CF ₃	OCH ₃	N
47	CF ₃	H	H	CF ₃	OCH ₃	N
48	CF ₂ H	H	H	CF ₃	OCH ₃	N

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No.	R ¹	R ²	R ⁵	R ³	R ⁴	Z
49	CO ₂ CH ₃	H	H	CF ₃	OCH ₃	CH
50	CO ₂ C ₂ H ₅	H	H	CF ₃	OCH ₃	CH
51	CO ₂ iC ₃ H ₇	H	H	CF ₃	OCH ₃	CH
52	NO ₂	H	H	CF ₃	OCH ₃	CH
53	SO ₂ CH ₃	H	H	CF ₃	OCH ₃	CH
54	SO ₂ N(CH ₃) ₂	H	H	CF ₃	OCH ₃	CH
55	Cl	H	H	CF ₃	OCH ₃	CH
56	N(CH ₃)SO ₂ CH ₃	H	H	CF ₃	OCH ₃	CH
57	OSO ₂ CH ₃	H	H	CF ₃	OCH ₃	CH
58	OSO ₂ N(CH ₃) ₂	H	H	CF ₃	OCH ₃	CH
59	CF ₃	H	H	CF ₃	OCH ₃	CH
60	CF ₂ H	H	H	CF ₃	OCH ₃	CH
61	CO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	N
62	CO ₂ C ₂ H ₅	H	H	CF ₂ H	OCH ₃	N
63	CO ₂ iC ₃ H ₇	H	H	CF ₂ H	OCH ₃	N
64	NO ₂	H	H	CF ₂ H	OCH ₃	N
65	SO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	N
66	SO ₂ N(CH ₃) ₂	H	H	CF ₂ H	OCH ₃	N
67	Cl	H	H	CF ₂ H	OCH ₃	N
68	N(CH ₃)SO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	N
69	OSO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	N
70	OSO ₂ N(CH ₃) ₂	H	H	CF ₂ H	OCH ₃	N
71	CF ₃	H	H	CF ₂ H	OCH ₃	N
72	CF ₂ H	H	H	CF ₂ H	OCH ₃	N
73	CO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	CH
74	CO ₂ C ₂ H ₅	H	H	CF ₂ H	OCH ₃	CH
75	CO ₂ iC ₃ H ₇	H	H	CF ₂ H	OCH ₃	CH
76	NO ₂	H	H	CF ₂ H	OCH ₃	CH
77	SO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	CH
78	SO ₂ N(CH ₃) ₂	H	H	CF ₂ H	OCH ₃	CH
79	Cl	H	H	CF ₂ H	OCH ₃	CH
80	N(CH ₃)SO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	CH

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No.	R ¹	R ²	R ⁵	R ³	R ⁴	Z
81	OSO ₂ CH ₃	H	H	CF ₂ H	OCH ₃	CH
82	OSO ₂ N(CH ₃) ₂	H	H	CF ₂ H	OCH ₃	CH
83	CF ₃	H	H	CF ₂ H	OCH ₃	CH
84	CF ₂ H	H	H	CF ₂ H	OCH ₃	CH
85	CO ₂ CH ₃	H	H	CF ₂ Cl	OCH ₃	N
86	CO ₂ C ₂ H ₅	H	H	CF ₂ Cl	OCH ₃	N
87	CO ₂ iC ₃ H ₇	H	H	CF ₂ Cl	OCH ₃	N
88	NO ₂	H	H	CF ₂ Cl	OCH ₃	N
89	SO ₂ CH ₃	H	H	CF ₂ Cl	OCH ₃	N
90	SO ₂ N(CH ₃) ₂	H	H	CF ₂ Cl	OCH ₃	N
91	Cl	H	H	CF ₂ Cl	OCH ₃	N
92	N(CH ₃)SO ₂ CH ₃	H	H	CF ₂ Cl	OCH ₃	N
93	OSO ₂ CH ₃	H	H	CF ₂ Cl	OCH ₃	N
94	OSO ₂ N(CH ₃) ₂	H	H	CF ₂ Cl	OCH ₃	N
95	CF ₃	H	H	CF ₂ Cl	OCH ₃	N
96	CF ₂ H	H	H	CF ₂ Cl	OCH ₃	N
97	CO ₂ CH ₃	3-F	H	Cl	OCH ₃	CH
98	CF ₂ CF ₃	H	H	CH ₃	OCH ₃	N
99	CF ₂ CF ₃	H	H	CH ₃	OCH ₃	N
100	SO ₂ C ₂ H ₅	H	H	F	OCH ₃	CH

Examples of preferred compounds (b) are
bromobutide

35 dimethenamid

isoxaben

propanil

glufosinate-ammonium

glyphosate

40 sulfosate

mefenacet

2,4-D

2,4-DB

2,4-DBEE

45 dichlorprop

dichlorprop-P

dichlorprop-P (2,4-DP-P)

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- fluroxypyr
MCPA
mecoprop
mecoprop-P
5 dicamba
bentazone
clomazone
diflufenican
sulcotrione
10 phenmedipham
thiobencarb
quinclorac
quinmerac
acetochlor
15 alachlor
butachlor
metazachlor
metolachlor
pretilachlor
20 butroxydim
caloxydim
clethodim
cycloxydim
sethoxydim
25 tralkoxydim
2-{1-[2-(4-chlorophenoxy)propyloxyimino]butyl}-3-hydroxy-5-(2H-tetrahydrothiopyran-3-yl)-2-cyclohexen-1-one
pendimethalin
acifluorfen-sodium
30 bifenox
fluoroglycofen-ethyl
fomesafen
lactofen
chlortoluron
35 cycluron
dymrone
isoproturon
methabenzthiazuron
imazaquin
40 imazethabenz-methyl
imazethapyr
bromoxynil
ioxynil
clodinafop
45 cyhalofop-butyl
fenoxyprop-ethyl
fenoxaprop-P-ethyl

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- haloxyfop-P-methyl
cinidon-ethyl
flumiclorac-pentyl
flumipropyn
5 fluthiacet-methyl
pyridate
clopyralid
bispyribac-sodium
KIH-8555
10 KUH-920
flumetsulam
metosulam
amidosulfuron
azimsulfuron
15 bensulfuron-methyl
chlorimuron-ethyl
chlorsulfuron
cinosulfuron
cyclosulfamuron
20 ethoxysulfuron
flazasulfuron
halosulfuron-methyl
HOE-107925
imazosulfuron
25 metsulfuron-methyl
nicosulfuron
primisulfuron
prosulfuron
pyrazosulfuron-ethyl
30 rimsulfuron
thifensulfuron-methyl
triasulfuron
tribenuron-methyl
atrazine
35 cyanazine
terbuthylazine
benazolin
benfuresate
cafenstrole
40 cinemthylin
ammonium-bentazone
cloquintocet
ET-751
F-8426
45 KPP-314

The following compounds are particularly preferred:

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- 2,4-D
dichlorprop-P
MCPA
mecoprop-P
- 5 dicamba
bentazone
diflufenican
sulcotrione
quinclorac
- 10 caloxydim
cycloxydim
sethoxydim
2-{1-[2-(4-chlorophenoxy)propyloxyimino]butyl}-3-hydroxy-5-(2H-tetrahydrothiopyran-3-yl)-2-cyclohexen-1-one
- 15 acifluorfen-sodium
fluoroglycofen-ethyl
bromoxynil
fenoxyprop-ethyl
cinidon-ethyl
- 20 amidosulfuron
bensulfuron-methyl
metsulfuron-methyl
nicosulfuron
pyrazosulfuron-ethyl
- 25 rimsulfuron
triasulfuron
tribenuron-methyl
atrazine
terbuthylazine
- 30 ammonium-bentazone
cloquintocet

The following compounds are very especially preferred:

- dichlorprop-P
- 35 mecoprop-P
ammonium-bentazone
bentazone
diflufenican
quinclorac
- 40 2-(1-[2-(4-chlorophenoxy)propyloxyimino]butyl)-3-hydroxy-5-(2H-tetrahydrothiopyran-3-yl)-2-cyclohexen-1-one
caloxydim
cycloxydim
sethoxydim
- 45 fluoroglycofen-ethyl
cinidon-ethyl
nicosulfuron

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pyrazosulfuron-ethyl
rimsulfuron
atrazine
terbuthylazine.

5

The present invention also relates to herbicidal compositions which comprise at least one herbicidally active amount of a sulfonylurea (a) of the above-described formula I or their environmentally compatible salts, a synergistically active amount of at least one above-described herbicidal compound (b) or its environmentally compatible salts, at least one liquid and/or solid carrier and, if desired, at least one adjuvant.

In the herbicidal mixtures and herbicidal compositions according to the invention, the sulfonylureas of the formula I or their environmentally compatible salts and the herbicidal compounds (b) or their environmentally compatible salts are used in such weight ratios that the desired synergistic effect is observed. The mixing ratios of sulfonylurea of the formula I and a herbicidal compound (b) are preferably 1 to 1:0.1 to 1:40, in particular 1:0.2 to 1:20, especially preferably 1:0.5 to 1:15.

The herbicidal mixtures and herbicidal compositions according to the invention which comprise the sulfonylureas of the formula I or their environmentally compatible salts of, for example, alkali metals, alkaline earth metals or ammonia and amines and the herbicidal compounds (b) or their environmentally compatible salts of, for example, alkali metals, alkaline earth metals or ammonia and amines are capable of effecting very good control of broad-leaved weeds and grass weeds in the crop rice without damaging the crop plants, an effect which is observed even when low rates of application are used.

Taking into consideration the versatility of the application methods, the herbicidal mixtures and herbicidal compositions according to the invention can also be employed in a further number of crop plants for eliminating undesirable plants. Suitable crops are, for example, the following:

Allium cepa, Ananas comosus, Arachis hypogaea, Asparagus officinalis, Beta vulgaris ssp. altissima, Beta vulgaris ssp. rapa, Brassica napus var. napus, Brassica napus var. napobrassica, Brassica rapa var. silvestris, Camellia sinensis, Carthamus tinctorius, Carya illinoensis, Citrus limon, Citrus sinensis, Coffea arabica (Coffea canephora, Coffea liberica), Cucumis sativus, Cynodon dactylon, Daucus carota, Elaeis guineensis, Fragaria vesca, Glycine max, Gossypium hirsutum,

(*Gossypium arboreum*, *Gossypium herbaceum*, *Gossypium vitifolium*),
Helianthus annuus, *Hevea brasiliensis*, *Hordeum vulgare*, *Humulus*
lupulus, *Ipomoea batatas*, *Juglans regia*, *Lens culinaris*, *Linum*
usitatissimum, *Lycopersicon lycopersicum*, *Malus* spp., *Manihot*
5 *esculenta*, *Medicago sativa*, *Musa* spp., *Nicotiana tabacum*
(*N.rustica*), *Olea europaea*, *Oryza sativa*, *Phaseolus lunatus*,
Phaseolus vulgaris, *Picea abies*, *Pinus* spp., *Pisum sativum*,
Prunus avium, *Prunus persica*, *Pyrus communis*, *Ribes sylvestre*,
Ricinus communis, *Saccharum officinarum*, *Secale cereale*, *Solanum*
10 *tuberosum*, *Sorghum bicolor* (s. *vulgare*), *Theobroma cacao*, *Trifo-*
lium pratense, *Triticum aestivum*, *Triticum durum*, *Vicia faba*,
Vitis vinifera, *Zea mays*,

In addition, the herbicidal mixtures and herbicidal compositions
15 according to the invention can also be used in crops which toler-
ate the action of herbicides due to breeding, including genetic
engineering methods.

The herbicidal mixtures and herbicidal compositions according to
20 the invention may be applied pre- or post-emergence. If the
active ingredients are less well tolerated by certain crop
plants, application techniques may be used in which the herbi-
cidal compositions are sprayed, with the aid of the spraying
equipment, in such a way that the active ingredients reach the
25 leaves of the sensitive crop plants as little as possible while
reaching the leaves of undesirable plants which grow underneath,
or the bare soil surface (post-directed, lay-by).

The compositions according to the invention can be applied, for
30 example in the form of ready-to-spray aqueous solutions, powders,
suspensions, also highly-concentrated aqueous, oily or other sus-
pensions or dispersions, emulsions, oil dispersions, pastes,
dusts, materials for spreading or granules, by means of spraying,
atomizing, dusting, spreading or pouring. The use forms depend on
35 the intended purposes; in any case, they should guarantee the
finest possible distribution of the active ingredients according
to the invention.

Suitable inert additives are mineral oil fractions of medium to
40 high boiling point, such as kerosene or diesel oil, furthermore
coal tar oils and oils of vegetable or animal origin, aliphatic,
cyclic and aromatic hydrocarbons, eg. paraffin, tetrahydronaph-
thalene, alkylated naphthalenes or their derivatives, alkylated
benzenes or their derivatives, methanol, ethanol, propanol, buta-
45 nol, cyclohexanol, cyclohexanone or strongly polar solvents such
as N-methylpyrrolidone or water.

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Aqueous use forms can be prepared from emulsion concentrates, suspensions, pastes, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of wetting agent, adhesive, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active ingredient, wetting agent, adhesive, dispersant or emulsifier and, if desired, solvent or oil, which are suitable for dilution with water.

10

Suitable surfactants are the alkali, alkaline earth and ammonium salts of aromatic sulfonic acids, eg. ligno-, phenol-, naphthalene- and dibutyl-naphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctylphenol, octylphenol or nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

Powders, materials for spreading, and dusts, can be prepared by mixing or concomitantly grinding the herbicidal mixture with a solid carrier.

Granules, eg. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredient onto solid carriers. Solid carriers are mineral earths such as silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders, or other solid carriers.

In general, the formulations comprise 0.01 to 95 % by weight, preferably 0.5 to 90 % by weight, of the herbicidal mixture.

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It may furthermore be advantageous to apply the herbicidal mixtures and herbicidal compositions according to the invention together in the form of a mixture with other crop protection agents, for example with agents for controlling pests or phytopathogenic fungi or bacteria. Also of interest is the miscibility with mineral salt solutions, which are employed for treating nutritional and trace element deficiencies. Non-phytotoxic oils and oil concentrates may also be added.

10 The rates of application of pure herbicidal mixture, ie. without formulation auxiliaries, are from 0.01 to 5 kg/ha, preferably 0.03 to 4 kg/ha, especially preferably 0.1 to 3.0 kg/ha, of active ingredient (a.i.), depending on the intended purpose, the season, the target plants and the growth stage.

15 The herbicidal compositions according to the invention are applied to the plants mainly by means of foliar sprays. They may be applied by customary spraying techniques using amounts of approximately 100 to 1000 l of spray mixture per ha, for example using water as the carrier. An application of the compositions in the so-called "low-volume" and "ultra-low-volume" method is also possible, as is their application in the form of so-called granules.

25 Use examples

The herbicide mixtures were applied post-emergence (foliar treatment), the sulfonylurea derivatives being applied in the form of 10 to 75 percent granules and the herbicidal compounds (b) in the formulation in which they exist as the commercial product.

The tests involved field trials with small plots at a sandy loam site (pH 6.2 to 7.0) or sandy clay (pH 5.0 to 6.7) site.

35 The weeds were present in different sizes and development stages, their height being, on average, 5 to 20 cm, depending on the plant habit.

The herbicidal compositions were applied alone and also jointly, in the latter case sometimes as a tank mix, sometimes as a ready-mix. This was done using water (350 l/ha) as the distribution vehicle, depending on the formulation of the active ingredients in the form of emulsions, aqueous solutions or suspensions. Application was effected with the aid of a mobile plot sprayer.

The test period extended over 3 to 8 weeks, and the stands were also observed at later dates.

The damage caused by the herbicidal compositions was assessed using a scale from 0 % to 100 % in comparison with untreated control plots. Thus, 0 means no damage, and 100 means complete destruction of the plants.

The examples which follow show the activity of the herbicidal compositions which can be used according to the invention without excluding the possibility of other uses.

In these examples, the method of S. R. Colby (1967): Calculating synergistic and antagonistic responses of herbicide combinations, Weeds 15, 20 et seq. was used to determine the value E which can be expected when an action of the individual active ingredients is merely additive.

The calculation was carried out using the formula

20

$$E = X + Y - \frac{XY}{100}$$

where

25

X = percentage activity using preparation A at a rate of application a

Y = percentage activity using preparation B at a rate of application b

E = expected activity (in %) caused by A + B at rate of application of a + b.

If the observed value exceeds the value E calculated using Colby's formula, a synergistic effect is present.

35

The herbicidal compositions according to the invention have a herbicidal activity which is higher than what can be expected when applying Colby's formula compared with the observed activities of the individual components used alone.

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